Crystal structure of mixed fluorites $Ca_{1-x}Sr_xF_2$ and $Sr_{1-x}Ba_xF_2$ and luminescence of Eu^{2+} in this crystals.

A.E. Nikiforov,

A.Yu. Zaharov, V.A. Chernyshev(Vladimir.Chernyshev@usu.ru),
M.Yu. Ougrumov, S.V. Kotomanov

Urals State University, Ekaterinburg, Russia

Abstract. Within the framework of the virtual crystal method implemented in the shell model and pair potential approximation the crystal structure of mixed fluorites $Ca_{1-x}Sr_xF_2$ and $Sr_{1-x}Ba_xF_2$ has been calculated. The structure of impurity center Eu^{2+} and the distance $E^{2+} - F^-$ in this crystals have been also calculated. The low level position of excited $4f^65d$ configuration of the Eu^{2+} ion has been expressed using phenomenological dependence on distance $Eu^{2+} - F^-$. The dependences of Stokes shift and Huang-Rhys factor on x have been received for yellow luminescence in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$. The value x, for which the e_g -level of Eu^{2+} ion will be in conduction band in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$ has been calculated.

1 Introduction

Fluorites CaF_2 , SrF_2 , BaF_2 and mixed crystals on their base attract attention of researchers more than four decades [1, 2, 3, 4, 5]. The crystals, doped by rare–earth ions, are good luminophors and are a basis for solid state lasers. The properties of luminescence and absorption depend on electronic structure of matrix crystal. The blue luminescence with zero phonon line (ZPL) is observed in $Ca_{1-x}Sr_xF_2 : Eu^{2+}$. The yellow luminescence without ZPL is observed in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$ at $x > 0,2$.

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2 Calculation of the crystal structure $Ca_{1-x}Sr_xF_2$ and $Sr_{1-x}Ba_xF_2$.

The method of virtual crystal have been implemented within the framework of the pair potential approximation and shell model. The method used has been described in previous work [6] . We have calculated the crystal structure of mixed fluorites $Ca_{1-x}Sr_xF_2$ and $Sr_{1-x}Ba_xF_2$ and of impurity center Eu^{2+} in this crystals. Dependence of a lattice constant of $Sr_{1-x}Ba_xF_2$ from x is given on fig.1.

The calculated dependence is in agreement with Wegard rule, though at medial concentrations is appreciable some difference from results of calculation. Similar dependence has been calculated for $Ca_{1-x}Sr_xF_2$.

3 Impurity ion Eu^{2+} in crystals $Ca_{1-x}Sr_xF_2$ and $Sr_{1-x}Ba_xF_2$

The luminescence and adsorption spectra of Eu^{2+} in $Ca_{1-x}Sr_xF_2$, $Sr_{1-x}Ba_xF_2$ deals with interconfigurational transitions between low excited levels of $4f^65d$ configuration and by $^8S(4f^7)$ ground state [5]. The ion Eu^{2+} is in center of cube formed by eight fluorines F^-. The splitting of $^8S(4f^7)$ ground state is small in cubic crystal field and does not exceed $0,2cm^{-1}$ [7]. Level $5d$ is enough feebly bound by with $4f^6$ orbitals in excited configuration $4f^65d$. The level splits to e_g and t_{2g} levels $12 - 16 \times 10^3 cm^{-1}$ [5]. The split considerably exceeds LS interaction in t_{2g} state and multiplet split of $4f^6$ levels [8]. Spectrum of the impurity ion is substantially defined by distance impurity ion–ligand. We have calculated the distance $Eu^{2+} - F^-$ in the crystals and then have calculated a phenomenological dependence of standing e_g and t_{2g} levels from the distance. Standing of e_g level in $Ca_{1-x}Sr_xF_2 : Eu^{2+}$, is expressed by dependence:

$$\nu(r) = C + \frac{A}{r^n} - \frac{B}{r^k} \qquad (1)$$

where $n = 12$, $k = 5$. The first term determines standing of $5d$ level in free ion Eu^{2+}, the second term determines shift of the level at placing Eu^{2+} in a crystal and third term deals with influence of crystal field on $t_{2g}-e_g$ splitting. Parameters A,B,C have been received by fitting the dependence to standing
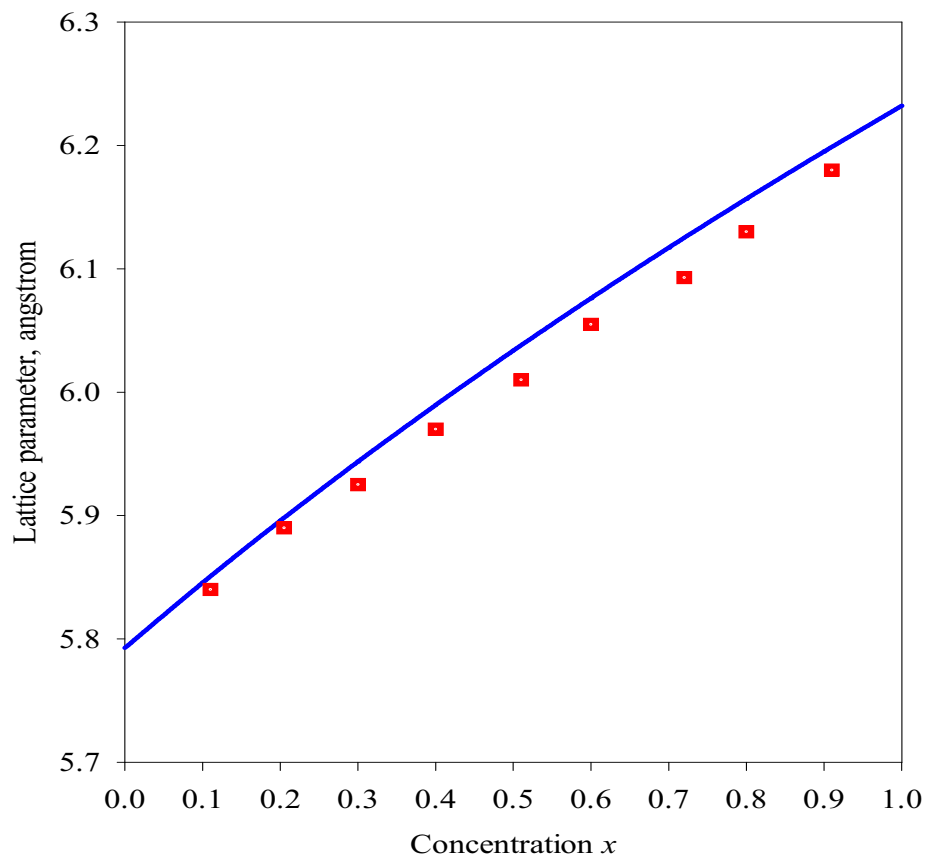
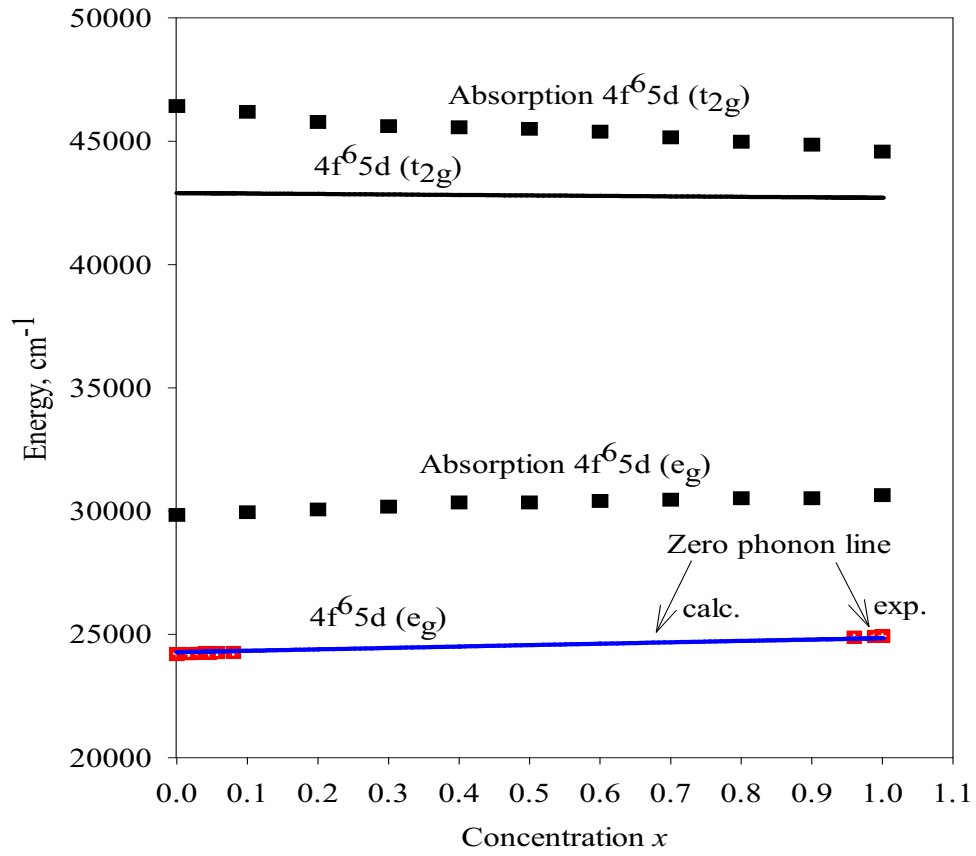Figure 1: The lattice constant of $Sr_{1-x}Ba_xF_2$ from x. Square symbol refer to experiment [1].

Figure 2: t_{2g} and e_g levels of Eu^{2+}. Square symbol refer to experiment[2].

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ZPL in CaF_2 and SrF_2 crystals [2] and $t_{2g} - e_g$ splitting in $MeF_2(Me = Ca, Sr, Ba)$ [3, 4]. The parameters are: $A = 439{,}7 \times 10^6 cm^{-1} \times \mathring{A}^{12}$, $B = 280 \times 10^5 cm^{-1} \times \mathring{A}^5$, $C = 36940 cm^{-1}$. The dependence of ZPL position from x we can receive using calculated distance $Eu^{2+} - F^-$ in $Ca_{1-x}Sr_xF_2 : Eu^{2+}$ at various x. It is possible to calculate the t_{2g} -level position by means of [7] taking into account that third term in [7] is equal to $6Dq$ (fig.2). The difference of the calculated t_{2g}-level position with short-wave adsorption peak can be explained by Stokes shift in adsorption.

The blue and yellow luminescence is observed in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$ for $x \in [0.2, 0.5]$ in intervals $430 - 450$ and $500 - 580$ nm. accordingly. The yellow luminescence at $x > 0.5$ is only observed [3]. Yellow luminescence due to interconfigurational transitions between levels of impurity exciton (which is formed by transition of electron to twelve nearby cations) and the ground state $^8S(4f^7)$ [3, 10] (fig.3). Position of e_g-level can be calculated in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$ using the expression (1). The top of valence band is formed by $2p$-states of fluorine in SrF_2 and BaF_2. The bottom of conduction band is formed by s-states of cation. Forbidden zone varies practically linearly in row CaF_2, SrF_2, BaF_2 [9]. The distance from e_g level to bottom of conduction band in $SrF_2 : Eu^{2+}$ was taken from McClure work [10]. Assuming the position of $2p$-states of fluorine does not change at replacing cations Sr^{2+} by Ba^{2+}, it is possible to calculate the changing of conduction zone bottom as a function from x. According to ours calculation, e_g-level will be in a conduction band for $x = 0.2$ in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$. The yellow luminescence will begin at this x in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$ [3].We have calculated configuration curves connected with A_{1g} -coordinate knowing how the energy of the crystal E depends on compression or expansion of a fluorine cube which surrounds Eu_{2+}. The deduced dependences $E(Q)$ (where Q-is the symmetrical coordinate) for $Sr_{1-x}Ba_xF_2 : Eu_{2+}$ are close to parabolic form $kQ^2/2$. Similar calculations was carried out for exciton state. The coefficient k dependences of the configurational curves on x are received: $k_{ES} = 33.95 - 5.26 * x$, $k_{GS} = 21.18 - 4.61 * x$, where $x \in [0, 1]$, (in $eV \times \mathring{A}^{-2}$). The coefficients k_ES and k_GS are decreasing at increasing the barium concentration. It compounded with the fact that the elastic modules BaF_2 are less than SrF_2. The fluorine cube is exposed to compression at formation of the exciton, the compression depends linearly on the concentration x in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$: $\triangle R = 0.143 + 0.036 * x$ (in $\mathring{A}$). We can receive the Stoks shift for yellow luminescence as we know k_GS and change of distance $Eu^{2+} - F^-$ at transition from exciton to the ground state:
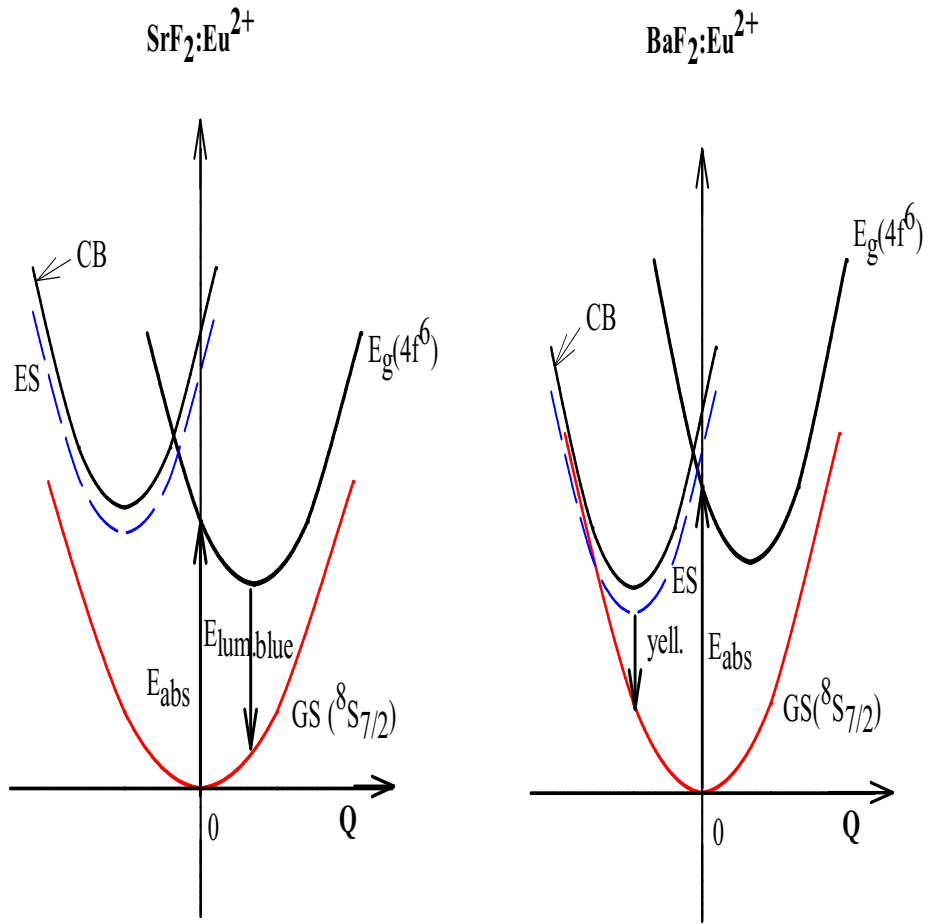
SrF$_2$:Eu^{2+}

BaF$_2$:Eu^{2+}

CB

ES

E$_g$(4f^6)

E$_{lum.blue}$

E$_{abs}$

GS (^{8}S$_{7/2}$)

0

Q

E$_g$(4f^6)

CB

ES

yell.

E$_{abs}$

GS(^{8}S$_{7/2}$)

0

Q

Figure 3: Configuration coordinate diagrams for describing of the blue and yellow luminescence in $CaF_2 : Eu^{2+}$ and $SrF_2 : Eu^{2+}$ [10]

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$E_s = 1090 * x + 5011$ (in cm^{-1}). The yellow luminescence have been observed in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$ at $\in [0.2, 1]$, and with increasing x its peak is shifting to the long-wave part of the spectrum [3]. According to our calculation the Stoks shift is increased on $800cm^{-1}$. We can estimate A_{1g} frequency of a cube from eight ions F^-:

$$\nu_{A_1g} = \sqrt{\frac{k_{GS}}{m_F}} \tag{2}$$

where m_F –a mass of the fluorine. According to our calculations $n = 547 - 63 * x$, (n in cm^{-1}). We can calculate Huang-Rhys factor for yellow luminescence as we know E_s and n. The factor is increasing from 9 to 12 at increasing x from 0 to 1 in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$.

4 Conclusion

The method of virtual crystal implemented in shell model and framework of pair potential approximation allows us to calculate the crystal structure and lattice constant for mixed fluorites $Ca_{1-x}Sr_xF_2$ and $Sr_{1-x}Ba_xF_2$. This method allows us to calculate the distance $Eu^{2+} - F^-$ in doped crystals $Ca_{1-x}Sr_xF_2 : Eu^{2+}$ and $Sr_{1-x}Ba_xF_2 : Eu^{2+}$. The low level position of excited $4f^65d$ configuration of an ion Eu^{2+} is expressed by phenomenological dependence on $Eu^{2+} - F^-$ distance . The dependences of Stokes shift and Huang-Rhys factor on x have been calculated for yellow luminescence in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$. According to our calculation the Stokes shift is increasing by $1000cm^{-1}$, the Huang-Rhys factor is increasing from 9 to 12 while x changes from 0 to 1. According to calculation the e_g level of Eu^{2+} ion will be within the conduction band for $x \geq 0.2$ in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$.

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